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Vibrational spectroscopic studies of $Sr[(CH_2)_2(NH_3)_2]_3P_4O_{12}.14H_2O$

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Abstract : IR and Raman spectra of $Sr[(CH_2)_2(NH_3)_2]_3P_4O_{12}.14H_2O$ have been recorded and analysed. The bands corresponding to $(CH_2)_2(NH_3)_2^{2+}$ and $P_4O_{12}^{4-}$ groups and water molecules are assigned. The $P_4O_{12}^{4-}$ ion in this compound is likely to have S_4 symmetry The absence of Fermi resonance suggests weak hydrogen bonds in the ethylenediammonium ion. Multiplicity of the stretching modes denotes the existence of atleast two crystallographically different water molecules in the compound The stretching frequencies of water molecules indicate that they are only weakly hydrogen bonded.

Keywords : Infrared spectra, Raman spectra.

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1. Introduction

Ethylenediamine forms very stable compounds by reacting with tetrametaphosphoric acid. X-ray studies of a number of such compounds have been reported [1,2]. From the crystal structure studies of $(CH_2)_2(NH_3)_2^{2+}$ (ethylenediammonium) and $P_4O_{12}^{4-}$ salts, it is observed that a number of conformations are possible for both these groups. The structural studies on $Sr[(CH_2)_2(NH_3)_2]_3P_4O_{12}.14H_2O$ have not yet been reported. The present study is an attempt to elucidate the structure of this compound and the nature of hydrogen bonding in it by an analysis of vibrational spectra of the compound.

2. Experimental

The sample was provided by Averbuch-Pouchot M T, Univ Joseph Fourier, Grenoble, France.

The compound in powder form was taken as a KBr pellet to record the IR spectrum using a Nicolet 170 SX FTIR spectrometer. For recording the Raman spectrum a Cary 82 spectrometer connected to the data system of a Nicolet 7000 series Fourier Transform (FT) IR spectrometer was used. A Spectra-Physics model 164–03 argon ion laser was used for the excitation and the spectra of powder samples were recorded using the 514.5 nm line with a resolution better than 2 cm^{-1}. Raman spectra in the range 50–2000 cm^{-1} and 2400–3800 cm^{-1} are presented in Figures 1 and 2 respectively. Figure 3 shows the IR spectrum of the studied compound in the range 400–4000 cm^{-1}.

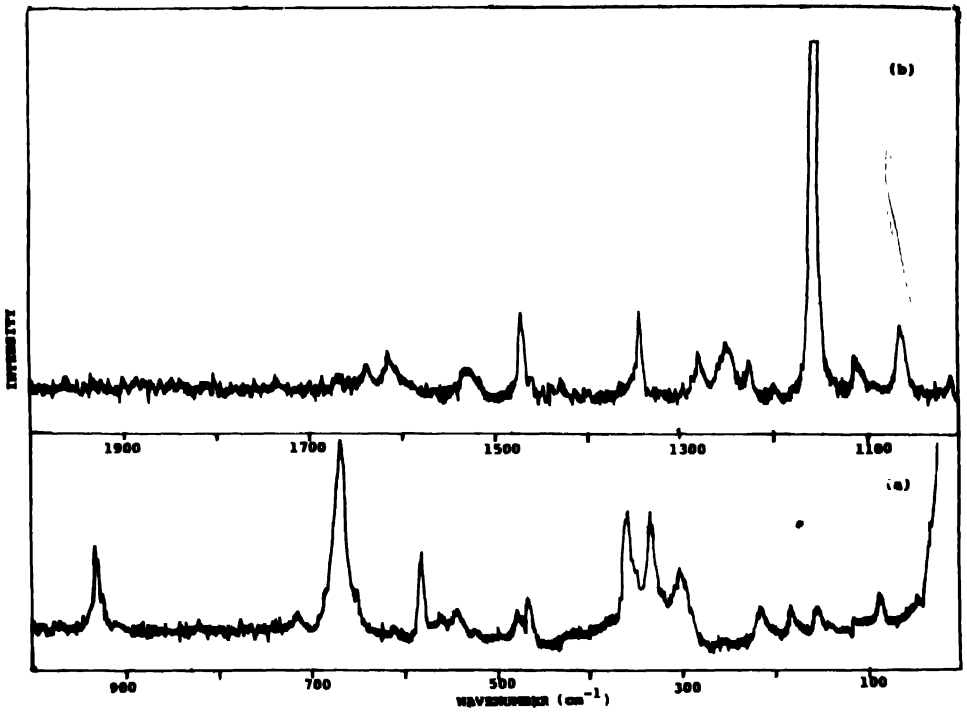

Figure 1. Raman spectra in the range (a) 50–1000 cm^{-1} and (b) 1000–2000 cm^{-1}.

3. Interpretation of the spectra

3.1. $(CH_2)_2(NH_3)_2^{2+}$ *vibrations:*

Assignments of the observed bands of ethylenediammonium ion (referred as eda) are carried out in terms of the vibrations of NH_3^+, CH_2 and skeletal modes.

The bands in the region 3220–2990 cm^{-1} are due to stretching modes of NH_3^+ [3–5]. The 3002 and 2990 cm^{-1} bands are assigned to $\nu_s NH_3^+$ since they are expected to be strong in Raman. Broad bands corresponding to $\nu_{as} NH_3^+$ and $\nu_s NH_3^+$ modes appear also in the IR

spectrum. The presence of strong hydrogen bonding in salts of this type may lead to considerable Fermi resonance between the NH stretching fundamentals and overtones and

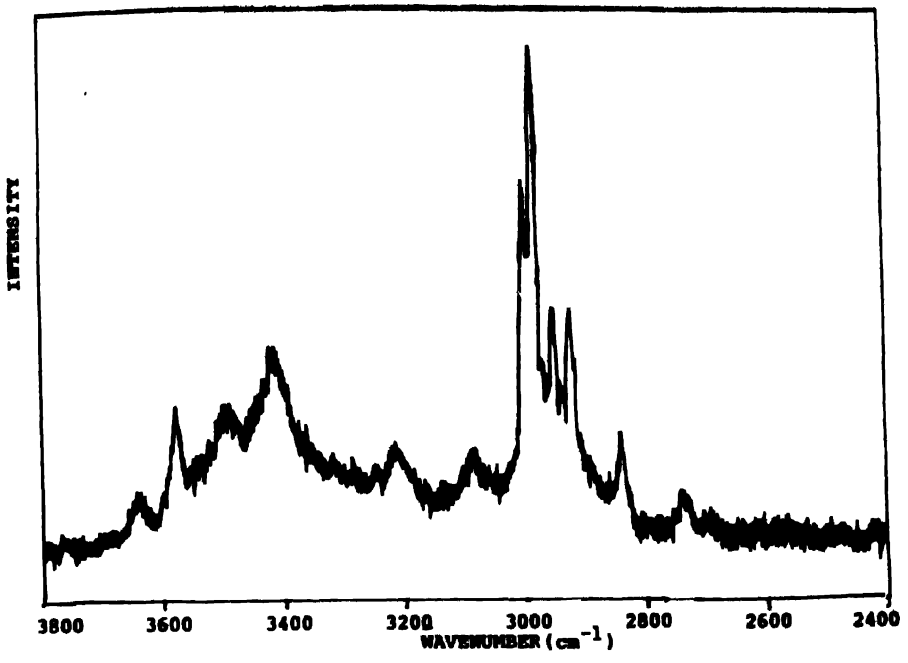

Figure 2. Raman spectrum in the range 2400–3800 cm^{-1}

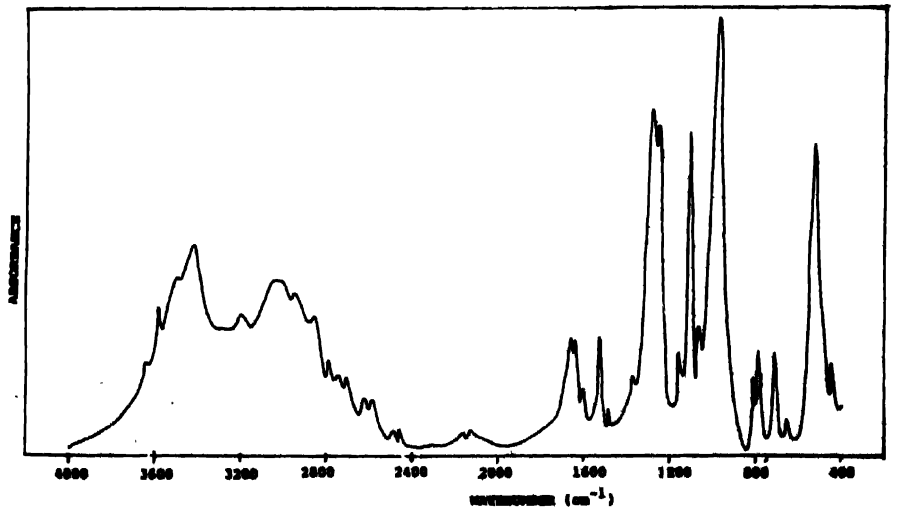

Figure 3. Infrared spectrum in the range 400–4000 cm^{-1}

combinations of the NH deformation modes [3]. Three groups of combination modes, designated as $\delta_{as}(NH_3^+) + \delta'_{as}(NH_3^+)$, $\delta_{as}(NH_3^+) + \delta_s(NH_3^+)$ and $\delta_s(NH_3^+) + \delta'_s(NH_3^+)$ can occur and they may shift their frequencies appreciably or gain in intensity by Fermi resonance. In the absence of Fermi resonance these modes can be observed [3] at

$$\delta_{as}(NH_3^+) + \delta'_{as}(NH_3^+) \quad 3180 - 3150\ cm^{-1},$$

$$\delta_{as}(NH_3^+) + \delta_s(NH_3^+) \quad \text{around } 3060\ cm^{-1},$$

$$\delta_s(NH_3^+) + \delta'_s(NH_3^+) \quad \text{around } 2940\ cm^{-1}$$

In the spectra of the title compound these bands are observed in the region of NH_3^+ and CH_2 stretching modes. The most intense bands have been somewhat arbitrarily chosen as the fundamentals. In the observed spectrum, all bands in this region, except the symmetric stretching NH_3^+ vibrations, are of medium or weak intensity. This indicates that hydrogen bonding in $(CH_2)_2(NH_3)_2^{2+}$ ion is weak in this compound. Moreover, the NH_3^+ stretching vibrations are at higher frequencies compound to those of (eda)$CdCl_4$ and are similar to those in (eda)$SnCl_6$ and (eda)$PtCl_6$ [3]. Hydrogen bonds are also weak in hexachloro salts.

$\nu_{as}CH_2$ and ν_sCH_2 appear in the region 2950–2840 cm^{-1} [3–5]. The lower frequency region of CH_2 stretching overlaps with the combination region. But combinations and overtones are usually weaker than fundamental vibrations and they seldom appear in Raman spectrum [6]. These bands are sharp in both Raman and IR spectra.

Oxton and Konp [3], and Powell [7] have noted the presence of bands of medium intensity in the 2100–1900 cm^{-1} region of the IR spectra of salts which contain the $C-NH_3^+$ grouping. These bands are identified as due to the combination modes involving NH_3^+ rocking vibrations. They appear as weak broad bands at 2160 and 2120 cm^{-1} in the IR spectrum.

The 1700–1600 cm^{-1} region is expected to contain $\delta_{as}NH_3^+$ and H_2O modes. It is difficult to assign these bands unambiguously. However, the bands at 1662 and 1640 cm^{-1} are stronger in IR than the band at 1605 cm^{-1}. The stretching bands of water fall in the region from 3640 to 3420 cm^{-1}; nearer to those of a free water molecule. These favour the assignment of 1605 cm^{-1} band to water bending vibration. Therefore, 1662 cm^{-1} and 1640 cm^{-1} bands are assigned to $\delta_{as}NH_3^+$ modes. The symmetric NH_3^+ mode is observed at 1530 cm^{-1} in both the spectra.

CH_2 bending vibrations give rise to the bands at 1470 cm^{-1} in Raman and 1480 cm^{-1} in IR [3,4]. Twisting and wagging modes of CH_2 are expected around 1340 cm^{-1}. This is observed as a single band in both Raman and IR spectra. The band around 1065 cm^{-1} in both Raman and IR is assigned to CN stretching mode. ν_{CC} and NH_3^+ rocking modes appear at lower frequencies than that of ν_{CN} [3]. But P–O–P stretching vibrations also appear in this region making an unambiguous assignment difficult.

The possible symmetries of ethylenediammonium ion are C_{2h} (trans structure) and C_2 (gauche structure) [3,8]. The bands in the region 1500–1250 cm^{-1} can indicate whether the ion has a trans or gauche structure. A strong or medium intense IR band at 1480 cm^{-1} suggests trans form of eda ion. For the gauche form this band is observed at 1460 cm^{-1} [8]. In this compound, only a weak IR band is observed at 1480 cm^{-1}. If the ion has a gauche conformation, bands will appear around 1454, 1394, 1365 and 1321 cm^{-1} in the IR spectrum. But only a very weak band is observed at 1365 cm^{-1} in $Sr(eda)_3P_4O_{12}.14H_2O$ in the IR. So from the observed spectra it is difficult to conclude the structure of ethylenediammonium ion in this compound.

3.2. $P_4O_{12}^{4-}$ *vibrations :*

The frequencies of the $P_4O_{12}^{4-}$ anion are assigned on the basis of the characteristic vibrations of PO_2^{2-} and POP groups [9–11]. The P–O bond in the PO_2^{2-} group is stronger than that in the POP bridge. Consequently, the vibrational frequencies of the PO_2^{2-} group are expected to be higher than those for the POP bridge. The asymmetric and symmetric stretching frequencies of PO_2^{2-} are generally observed in the regions 1340–1220 and 1160–1100 cm^{-1} respectively [9–12]. The Raman lines at 1280, 1250 and 1225 cm^{-1} and the IR lines at 1285 and 1250 cm^{-1} are assigned to ν_{as} PO_2^{2-} The stronger band at 1155 cm^{-1} and the weak band at 1110 cm^{-1} in Raman and the IR bands at 1155 and 1105 cm^{-1} are due to ν_s PO_2^{2-}. The band at 930 cm^{-1} in Raman and 980 cm^{-1} in IR are assigned as the asymmetric POP stretching mode and the bands at 815, 790, 710 and 660 cm^{-1} in IR and 715 and 670 cm^{-1} in Raman to symmetric POP stretching modes. The bending modes of PO_2^{2-} and POP are assigned in regions 580–524 cm^{-1} and 360–220 cm^{-1} respectively. The Raman bands at 580 and 540 cm^{-1} and the IR band at 524 cm^{-1} are due to δ PO_2^{2-}. For the POP bridge these modes are at 360, 302 and 220 cm^{-1} in the IR.

The possible symmetries of the $P_4O_{12}^{4-}$ anion are C_i, C_{2h}, S_4 and D_{2d} [9,10,13]. Coincidence of most of the vibrational modes of the $P_4O_{12}^{4-}$ ion in Raman and IR spectra indicates a non-centrosymmetric structure for the ion in this compound. Hence, the symmetry of the anion must be S_4 or D_{2d} . S_4 symmetry is characterised by the presence of an IR band near or above 800 cm^{-1} with another band between 750 and 700 cm^{-1} and a Raman band below 700 cm^{-1} [14]. The bands observed in the ν_s POP region of $Sr(eda)_3P_4O_{12}.14H_2O$ are in agreement with this, indicating that S_4 can be the symmetry of the $P_4O_{12}^{4-}$ ion in this compound.

The metal-oxygen stretching vibrations [15] occur in the POP bending region and therefore it is difficult to assign them unambiguously.

3.3. H_2O *vibrations :*

The vibrational frequencies of a free water molecule are at 3756 (ν_{as}), 3652 (ν_s) and 1595 (δ_{as}) cm^{-1} [16]. Depending on the strength of hydrogen bonding, the stretching modes will

Table 1. Spectral data (cm^{-1}) and band assignments.

Raman	IR	Assignments
3640 w 3580 m 3500 mbr 3420 m	3640 m 3580 m 3500 w 3420 s	ν_{as} and ν_s H_2O
3220 w 3090 w	3200 wbr	$\nu_{as}NH_3^+$
3002 s 2990 s	3020 mbr	$\nu_{as}NH_3^+$
2950 m	2940 m	ν_{as} CH_2
2920 m 2840 w	2860 m	ν_s CH_2
2740 vw	2790 vw 2740 vw 2700 vw 2620 w 2580 w 2480 vw 2455 w	Combinations and overtones
	2160 wbr 2120 wbr	Combinations involving NH_3^+ rock
1665 vw 1640 vw	1662 m 1640 m	$\delta_{as}NH_3^+$
1615 vwbr	1605 vw	δH_2O
1530 vw	1530 m	δ_s NH_3^+
1470 w	1480 vw	δCH_2
1342 w	1365 vw	Twisting and wagging of CH_2
1280 w 1250 wbr 1225 w	1285 vs 1250 vs	$\nu_{as}PO_2^{2-}$
1155 vs 1110 wbr	1155 m 1105 vs	$\nu_s PO_2^{2-}$
1065 w	1068 m	ν_{CN}
930 w	980 vs 815 m 790 m	ν_{as} POP
715 vw 670 m	710 m 660 vw	ν_s POP

Table 1. *(Contd.)*

Raman	IR	Assignments
580 w		
540 vw	524 vs	δPO_2^{2-}
475 vw		
465 vw	455 vw	NH_3^+ torsion
360 m		
335 m		δ POP and metal-oxygen
302 w		stretching
220 vw		
180 vw		
155 vw		Lattice modes
90 vw		

ν_s – symmetry stretching, ν_{as} – asymmetric stretching
δ_s – symmetric bending, δ_{as} – asymmetric bending
vs – very strong, s – strong, m – medium, mbr – medium broad, vw – very weak, w – weak, vwbr – very weak broad, wbr – weak broad.

shift to lower wavenumbers and bending modes to higher wave numbers [16]. The bands in the region 3640–3420 cm^{-1} are due to the stretching vibrations of H_2O and the bands at 1615 cm^{-1} in Raman spectrum and 1605 cm^{-1} in the IR are due to the bending vibrations of H_2O. The stretching and bending modes of water indicate that water molecules form only weak hydrogen bonds in the compound. The four bands in the stretching region and the broad bending mode show that at least two crystallographically different water molecules exist in the crystal.

4. Conclusions

1 The absence of Fermi resonance suggests weak hydrogen bonds in the eda ion.

2 The $P_4O_{12}^{4-}$ ion in the compound is likely to have S_4 symmetry.

3 Atleast two crystallographically different water molecules are present in the compound. The stretching frequencies of water molecules indicate that they are only weakly hydrogen bonded.

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